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(54) **GAS GENERATOR FOR AIR BAG**

(57) The air bag gas generating composition according to the present invention comprises, as active components, (1) biscarbamoylhydrazine as a gas generating base, (2) an oxohalogen acid salt as an oxidizing agent, (3) a nitrate as an oxidizing agent, and (4) a burning catalyst. The air bag gas generating composition according to the present invention has advantageous characteristics of appropriate burning performance, low burning temperature, low concentration of the toxic components such as CO and NOx in the gas generated by the combustion, a low concentration of the suspended particulate matter released, good heat stability, and remarkably higher safety than conventional azide-based and azide-free gas generating compositions.



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## Description

### Technical Field

The present invention relates to an air bag gas generating composition.

The air bag gas generating composition according to the present invention possesses advantageous characteristics of suitable burning performance, low burning temperature, low concentration of toxic components such as CO and NOx in the gas generated by the combustion, low concentration of the suspended particulate matter released, good heat stability, and remarkably higher safety than conventional azide-based and azide-free gas generating compositions.

### Background Art

As the requirements concerning driving safety become more rigorous, the demand for air bag systems is greatly increasing. When a car travelling at high speed is in a crash, the air bag system inflates a nylon bag (air bag) stowed in the steering wheel assembly, the dashboard or the like to thereby protect the occupants from being injured or killed by the impact against the interior of the car. The bag is inflated with a gas generated by the combustion of a gas generating composition held in the inflator (gas generating vessel) of said system.

The air bag gas generating composition is required to have a number of performance characteristics, among which the following six are important requirements.

First, the gas generating composition should show appropriate burning velocity in the inflator. In the air bag system, a sensor detects the impact to the automobile and determines whether the impact is caused by a real crash, and if so, the gas generating composition in the inflator is ignited and emits gas to inflate the air bag which protects the bodies of the occupants, in particular their heads. When an automobile is in a crash, the heads of the occupants start to move after a certain period of time, and thus the air bag must inflate in accordance with the movement of the heads. Therefore, too high or too low a burning velocity is not desirable.

The second requirement is low burning temperature. If the burning temperature of the gas generating composition is high, the gas released into the bag is also hot enough to impair the bag. Further, gas that leaks from such an impaired bag may cause the occupants to sustain burns. Usually, solid by-products from the combustion is removed by a filter provided between the inflator and bag and is not contained in the released gas. However, if the burning temperature is high, the solid by-products evaporate and are released into the bag, in which the vapor condenses and forms suspended particulate matter which may damage the bag.

The third requirement is low concentration of toxic components such as CO and NOx in the gas generated by the combustion. For reducing the impact on the occupants smashing into the air bag, the bag deflates to some extent immediately after the inflation, releasing part of the gas inside the car. If the concentration of the active components is high, the occupants are likely to be poisoned.

The fourth requirement is good heat stability. Generally, the gas generating composition should have a long life of at least ten and several years. It is essential that the gas generating composition does not decompose at a temperature to which automobiles are exposed, especially at a high temperature in summer.

The fifth requirement is high safety of the starting materials, intermediates and final product. Among the safety measures, it is important that the shock ignitability (sensitivity to shock ignition) is low. High shock ignitability involves a high risk in handling and a high possibility of detonation in the course of production, e.g., in the mixing or molding process. Therefore, it may cause damage to the equipment around the air bag and the environment, and moreover, may mortally wound the occupants.

The sixth requirement is low toxicity. If the starting materials, intermediates and final product of the gas generating composition are highly toxic, problems may arise at the time of production and discard.

Conventionally, azide-based gas generating compositions comprising sodium aside as the gas generating base are generally used as the air bag gas generating composition. Although the aside-based gas generating composition is a good gas generating composition which fulfills the above first to fourth requirements, said composition a drawback of high ignitability, requiring careful handling in the production and other processes. Further, since sodium aside is toxic, handling thereof necessitates protection equipment. Also, use of sodium azide is disadvantageous in that waste water from operations using sodium azide requires a disposal plant for exclusive use.

Recently, people have acknowledged the great importance of environmental protection and safety of operators and users. The azide-based gas generating compositions are not preferred due to the above drawbacks. Accordingly, an azide-free gas generating base substituting for sodium azide is earnestly demanded to be developed.

Known substitutes for the azide-based gas generating composition are, for example, azide-free gas generating compositions containing a nitrogen-containing organic compound such as azodicarbonamide (ADCA) or the like and an oxidizing agent (Japanese Unexamined Patent Publications Nos. 32,689/1994, 32,690/1994 and 227,884/1994, etc.). Said gas generating composition shows appropriate burning velocity which is equivalent to that of the conventional aside-based gas generating compositions, have low shock ignitability, and are remarkably low in detonativity and toxic-

ity. Further, the burning temperature and the concentration of active components in the gas such as CO and NOx are low enough for practical use. However, further reduction in said concentration is hoped for. In addition, the heat stability of said azide-free gas generating compositions is demanded to be further improved.

Japanese Unexamined Patent Publication No. 300,383/1995 discloses a composition comprising as active components biscarbamoylhydrazine (hydrazodicarbonamide) and an oxohalogen acid salt, as a gas generating composition with excellent heat stability. However, said composition shows high detonativity, and further has drawbacks of high burning temperature and production of a great amount of potassium chloride as a by-product, which readily form suspended particulate matter.

DE-A-19,516,818 discloses a gas generating composition comprising, as active components, biscarbamoylhydrazine, an oxidizing agent such as an oxohalogen acid salt, nitrate or the like, and a coolant such as sulfate hydrate, nitrate hydrate, carbonate, carbonate hydrate, hydroxide, hydroxide hydrate or the like of a metal of the III, IV, V or VI period. However, said gas generating composition is not satisfactory in burning performance and is likely to cause incomplete combustion, which results in a serious defect that the air bag does not inflate immediately after the crash.

Disclosure of the Invention

An object of the present invention is to provide an air bag gas generating composition which has burning velocity and burning temperature equivalent to or more suitable than those of conventional azide-based or aside-free gas generating compositions, much lower concentration of toxic components such as CO and NOx in the gas, and remarkably excellent heat stability.

Another object of the present invention is to provide an air bag gas generating composition which is remarkably lower in shock ignitability, detonativity and toxicity than the above azide-free gas generating composition, and low in the concentration of suspended particulate matter released.

A further object of the present invention is to provide an air bag gas generating composition which does not cause incomplete combustion.

Other features of the present invention will become apparent from the following description.

The present invention provides an air bag gas generating composition comprising, as active components, (1) biscarbamoylhydrazine as a gas generating base, (2) an oxohalogen acid salt as an oxidizing agent, (3) a nitrate as an oxidizing agent, and (4) a burning catalyst.

The present invention also provides an air bag gas generating composition comprising, as active components, (1) biscarbamoylhydrazine as a gas generating base, (2) an oxohalogen acid salt or a nitrate as an oxidizing agent, and (3) a burning catalyst.

The gas generating composition of the present invention meets all of the first to sixth requirements mentioned above. Said gas generating composition does not cause incomplete combustion, shows burning velocity and burning temperature equivalent to or more appropriate than those of the conventional azide-based or azide-free gas generating compositions, and is still lower in the concentration of toxic components such as CO and NOx in the gas, remarkably low in shock ignitability, detonativity and toxicity, low in the concentration of the suspended particulate matter released, and remarkably excellent in heat stability.

Biscarbamoylhydrazine (also called biurea or hydrazodicarbonamide) used as the gas generating base of the gas generating composition of the present invention has been mainly used as a starting material for ADCA. Other use of biscarbamoylhydrazine is found only in a cell nucleating agent for adjusting the shape of foam cells when foaming a synthetic resin with high chemical resistance and heat resistance (e.g., vinyl chloride resin) using ADCA.

Since biscarbamoylhydrazine has higher heat stability than ADCA and remarkably high stability to alkali, use thereof advantageously broadens the selection range of the oxidizing agent, burning catalyst and the like, and contributes to the significant improvement in the heat stability of the gas generating composition of the present invention. Further, biscarbamoylhydrazine is very low in toxicity and free from a risk of explosion, and thus contributes to the improvement in the safety of the gas generating composition of the present invention.

According to the present invention, commercially available biscarbamoylhydrazine can be used as such. The particle size of biscarbamoylhydrazine is not limited specifically, and can be properly selected from a wide range in accordance with, for example, the amount used, kinds and proportions of other components to be used in combination, volume of the air bag and other conditions.

Biscarbamoylhydrazine forms crystals of scale or plate shape, in which the binding force between the particles is weak. Therefore, the moldability in the process of preparation may sometimes be unsatisfactory. According to the present invention, for reducing the possibility of unsatisfactory moldability, it is desirable to use the undermentioned binder in an amount of about 2.0 to about 10 wt. parts, preferably about 3 to about 6 wt. parts, which is greater than the amount used in conventional azide-free gas generating composition (about 0.5 to about 2.0 wt. parts), or to use biscarbamoylhydrazine as modified and/or finely ground in combination with the same amount of binder as in the conventional composition. Biscarbamoylhydrazine can be modified, for example, by surface-treating biscarbamoylhydrazine with an inorganic surface treating agent or by surface-coating biscarbamoylhydrazine with a hydrophilic polymeric compound

or a crosslinked product thereof.

First, the process of surface-treating biscarbamoylhydrazine with an inorganic surface treating agent is described. Known inorganic surface treating agents are usable, among which water-soluble metal salts are preferred. Specific examples of the water-soluble metal salts are chlorides such as $AlCl_3$, $CoCl_2$, $ZrCl_4$, $SnCl_2$, $SnCl_4$, $TiCl_3$, $TiCl_4$, $FeCl_2$, $FeCl_3$, $CuCl_2$, $NiCl_2$ and $MoCl_5$, nitrates of metals such as Al, Co, Zr, Sn, Ti, Fe, Cu, Ni and Mo, silicates such as $Na_4SiO_4$ and $K_2Si_4O_9$, $ZrCl_2O$, $NaAlO_2$ and the like, among which $AlCl_3$, $NaAlO_2$, $FeCl_2$ and $FeCl_3$ are preferred, and $NaAlO_2$ are particularly preferred. These surface treating agents may be used singly or as a mixture of two or more. The amount of the surface treating agent is not limited specifically, and can be properly selected from a wide range in accordance with the kind of the surface treating agent, kinds and amounts of the other components of the gas generating composition than the modified biscarbamoylhydrazine, contemplated performance characteristics of the resulting gas generating composition. Generally, however, the amount of the surface treating agent is about 0.01 to about 5 wt.%, preferably 0.1 to 2 wt.% of the total weight of biscarbamoylhydrazine to be surface-treated.

The surface treatment can be carried out by a conventional method.

For example, when a water-soluble metal salt is used as the surface treating agent, modified biscarbamoylhydrazine can be prepared by mixing biscarbamoylhydrazine with the water-soluble metal salt in water, neutralizing the mixture and fractionating and drying biscarbamoylhydrazine. The pH adjustor used for neutralization is not limited specifically, and may be a known acid or alkali. Examples of the acid are inorganic acids such as hydrochloric acid, sulfuric acid, oxalic acid, nitric acid and phosphoric acid, organic acids such as acetic acid, and the like. Examples of the alkali are sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium hydrocarbonate, potassium hydrocarbonate, ammonia, etc. Biscarbamoylhydrazine is dried usually at about 0 to about 250°C, preferably about 50 to about 150°C, taking into consideration the fact that the heat decomposition temperature of biscarbamoylhydrazine is about 250 to about 260°C. The drying is carried out usually under normal pressure, but may be done under reduced pressure. Biscarbamoylhydrazine may be finely ground or recrystallized before being surface-treated.

Next, the process for surface-coating biscarbamoylhydrazine with a hydrophilic polymeric compound or a crosslinked product thereof. The process for surface-coating with a hydrophilic polymeric compound comprises, for example, adding the hydrophilic polymeric compound to an aqueous solution or dispersion of biscarbamoylhydrazine, followed by mixing. Since biscarbamoylhydrazine is low soluble in water, an aqueous dispersion is preferred from the viewpoint of the efficiency and the like. At the time of mixing, the mixture may be heated if necessary.

The hydrophilic polymeric compound is not limited specifically, and any of conventional ones can be used. Examples are cellulose compounds such as carboxymethyl cellulose, modified carboxymethyl cellulose, hydroxymethyl cellulose and microcrystalline cellulose, polyvinyl alcohols such as completely saponified polyvinyl alcohol and partially saponified polyvinyl alcohol, starches such as soluble starch, and the like. These hydrophilic polymeric compound can be used singly or as a mixture of two or more.

The hydrophilic polymeric compound can be added as such or in the form of an aqueous solution. The amount of the hydrophilic polymeric compound is not limited specifically and can be properly selected from a wide range. Usually, however, a suitable amount is about 0.1 to about 5 wt.%, preferably about 0.5 to about 3 wt.% based on the amount of biscarbamoylhydrazine to be treated.

Biscarbamoylhydrazine can be surface coated with a crosslinked product of the hydrophilic polymeric compound, for example, by adding the hydrophilic polymeric compound, an olefin and a water-soluble polymerization initiator to an aqueous solution or dispersion of biscarbamoylhydrazine, and stirring the mixture with heating.

Examples of the hydrophilic polymeric compound are as mentioned above.

Any of the conventional olefins having a polymerizable double bond can be used. Examples are unsaturated carboxylic acids such as acrylic acid, methacrylic acid, maleic acid and itaconic acid, vinyl-containing compounds such as vinyl acetate and divinyl benzene, and the like. Also usable are (meth)acrylic acid alkyl esters whose alkyl moiety is a straight- or branched-chain alkyl group having about 1 to about 4 carbon atoms. Examples of the (meth)acrylic acid alkyl esters are ethyl (meth)acrylate, methyl (meth)acrylate and the like. Further, (meth)acrylic acid aryl esters such as phenyl (meth)acrylate are also usable. These olefins can be used singly or as a mixture of two or more. The amount of the olefin is not limited specifically and can be properly selected from a wide range, but is usually about 0.1 to about 3 wt.%, preferably about 0.5 to about 1 wt.% based on the amount of biscarbamoylhydrazine to be treated.

The water-soluble polymerization initiator is not limited specifically, and any of those conventionally known are usable. Examples are hydroxy peroxides such as cumene hydroxy peroxide, water-soluble potassium peroxosulfate, ammonium peroxosulfate, hydrogen peroxide, azobisisobutyronitrile, azobiscyclohexanecarbonyl, azobisvaleric acid, 2,2'-azobis(2-amidinopropane)• dihydrochloride and the like. These water-soluble polymerization initiators can be used singly or as a mixture of two or more. The amount of the water-soluble polymerization initiator is not limited specifically and can be properly selected from a wide range, but usually about 0.01 to about 5 wt.%, preferably about 0.05 to about 1 wt.% based on the amount of the olefin.

The temperature for heating is not limited specifically, but usually about 50 to about 90°C, preferably about 80°C. The mixing time is not limited specifically, and usually about 30 minutes to about 5 hours, preferably about 1 to about 2 hours.

After the treatment, the modified biscarbamoylhydrazine is isolated by a conventional method such as filtration or centrifugation, and dried.

Next, the process for finely grinding biscarbamoylhydrazine is described. Powdery biscarbamoylhydrazine is ground with a high pressure grinder to give a fine powder.

The high pressure grinder are, for example, those having a system which comprises blowing high-pressure air into the interior of the grinder from at least two directions of the sides of the machine in order to make an air stream which grinds the powder, and collecting the finely ground powder suspended with the machine by the air pressure. Specific examples are a counter jet mill (product of Alpine Co., Ltd., a Netherlands company), a cross jet mill (product of Kurimoto, Ltd.), and the like.

According to the present invention, the air pressure and grinding time of the high pressure grinder can be properly selected to obtain a desired fine powder of biscarbamoylhydrazine. It is suitable that the air pressure be usually about 3 to about 8 kgf/cm$^2$, preferably about 5 to about 7 kgf/cm$^2$, and that the grinding time be usually about 5,000 to about 20,000 rpm, preferably about 10,000 to about 15,000 rpm.

In the present invention, it is suitable that biscarbamoylhydrazine finely ground by the above process have an average particle size of usually 20 $\mu$m or less and a BET specific surface area of 0.5 m$^2$/g or more, preferably an average particle size of 10 $\mu$m or less and a BET specific surface area of 5 m$^2$/g or more. If the average particle size greatly exceeds 20 $\mu$m and/or the BET specific surface area is far below 0.5 m$^2$/g, the moldability of biscarbamoylhydrazine is insufficiently improved and the pellets prepared therefrom may have a lower strength, like in the case of unground biscarbamoylhydrazine. As used herein, the average particle size is measured with a laser diffraction particle size distribution measuring device (product of Horiba, Ltd.). The BET specific surface area is measured using a BET specific surface area measuring device (product of Shimazu, Corp.).

The thus obtained finely ground biscarbamoylhydrazine can be used as a gas generating base without further processing, but is more preferably used in the form of granules since the moldability and the burning performance of the gas generating composition will be further improved. A suitable grain size of the granules is usually about 0.05 to about 1 mm, preferably about 0.1 to about 0.5 mm. The granulation can be carried out by a conventional process, for example, by optionally adding a suitable amount of water or warm water to the finely ground biscarbamoylhydrazine, forming the mixture into granules and drying the granules. The formation of the granules can be attained by a conventional process, for example, using an extrusion granulating machine of various types such as screw type, roll type, blade type, self-molding type and ram type. Rolling, spray drying and other granulation processes can be also employed.

As the oxidizing agent, another active component of the gas generating composition of the present invention, a nitrate or oxohalogen acid salt is used singly, or a nitrate and oxohalogen are used in combination.

Examples of the nitrate are alkali metal salts such as lithium nitrate, sodium nitrate and potassium nitrate, alkali earth metal salts such as magnesium nitrate, barium nitrate and strontium nitrate, ammonium salts such as ammonium nitrate, and the like. Among them, alkali metal salts and alkali earth metal salts are preferred, and potassium nitrate and strontium nitrate are particularly preferred.

Conventional oxohalogen acid salts are usable. Examples are perhalogenates, halogenates and the like. Examples of useful perhalogenates are alkali metal salts such as lithium perchlorate, potassium perchlorate, sodium perchlorate, lithium perbromate, potassium perbromate and sodium perbromate, alkali earth metal salts such as magnesium perchlorate, barium perchlorate, calcium perchlorate, magnesium perbromate, barium perbromate and calcium perbromate, ammonium salts such as ammonium perchlorate and ammonium perbromate, and the like. Examples of useful halogenates are alkali metal salts such as lithium chlorate, potassium chlorate, sodium chlorate, lithium bromate, potassium bromate and sodium bromate, alkali earth metal salts such as magnesium chlorate, barium chlorate, calcium chlorate, magnesium bromate, barium bromate and calcium bromate, ammonium salts such as ammonium chlorate and ammonium bromate, and the like. Among them, alkali metal salts of halogen acids and perhalogen acids are preferred, and potassium perchlorate and potassium chlorate are particularly preferred.

Commercially available nitrates and oxohalogen acid salts can be used as such. The shape, particle size and the like are not limited specifically, and can be properly selected in accordance with, for example, the amount of the oxidizing agent used, proportions to other components, and volume of the air bag and other conditions.

The oxidizing agent, whether it is the nitrate or oxohalogen acid salt alone or a combination of the nitrate or oxohalogen acid salt, is used usually in a stoichiometric amount sufficient to completely oxidize and burn biscarbamoylhydrazine, calculated on the basis of the amount of oxygen. The amount of the oxidizing agent can be properly selected from a wide range, since the burning velocity, burning temperature (gas temperature), composition of the combustion gas, etc. can be adjusted as desired by suitably changing the proportions of the gas generating base and oxidizing agent. For example, the nitrate, oxohalogen acid salt or a combination of the nitrate and oxohalogen acid salt is suitably used in a proportion of about 10 to about 400 wt. parts, preferably about 100 to about 240 wt. parts, per 100 wt. parts of biscarbamoylhydrazine. When the nitrate and oxohalogen acid salt are used in combination, the proportions of the two oxidizing agents are not limited specifically and can be properly selected. If the proportion of the oxohalogen acid salt is greater than the amount mentioned above, high burning temperature results, which entails a risk of explosion and the production of a large amount of halides of alkali metals which form suspended particles, such as potassium chloride.

Thus, the proportion above said range is not preferred.

In the air bag gas generating composition according to the present invention, the burning catalyst, one of the active components, is considered to serve mainly to decrease the burning temperature and reduce the concentrations of CO and/or NOx in the gas. Usable burning catalysts include oxides of the metals of the 4th to 6th periods in the periodic table, oxygen-containing metallic compounds which form said metal oxides when heated, heteropolyacids and the like.

Specific examples of the oxides of metals of the 4 to 6 periods in the periodic table are copper oxide, nickel oxide, cobalt oxide, iron oxide, chromium oxide, manganese oxide, zinc oxide, calcium oxide, titanium oxide, vanadium oxide, cerium oxide, holmium oxide, ytterbium oxide, molybdenum oxide, tungsten oxide, antimony oxide, tin oxide, titanium oxide and the like. Among them, copper oxide, nickel oxide, cobalt oxide, molybdenum oxide, tungsten oxide, iron oxide, tin oxide, zinc oxide and chromium oxide are preferred, and CuO, CoO, NiO, $Ni_2O_3$, $MoO_3$, $WO_3$, $Cr_2O_3$, $TiO_2$, SnO, ZnO and $Fe_2O_3$ are particularly preferred. These metal oxides include hydrates thereof, for example, hydrates of tungsten oxide, such as $WO_3 \cdot H_2O$. It is preferred that the metal oxide have a BET specific surface area of at least 5 $m^2/g$, more preferably at least 10 $m^2/g$, still more preferably at least 40 $m^2/g$. Among the above mentioned metal oxides, MoO, $WO_3$ and the like have an advantageous characteristic of the capability of reducing the CO concentration and NOx concentration at the same time.

The oxygen-containing metal compound which form, when heated, the oxides of metals of the 4th to 6th periods in the periodic table are not limited specifically, and those conventionally known can be used. For example, oxygen-containing molybdenum compounds which form $MoO_3$ when heated include Group VIII metal salts of molybdic acid such as cobalt molybdate and nickel molybdate, molybdic acid, molybdenum hydroxide, and the like. Oxygen-containing tungsten compounds which form $WO_3$ when heated include, for example, tungstic acid, metal salts thereof, and the like. Examples of the metal salts of tungstic acid include alkali metal halts such as lithium tungstate, potassium tungstate and sodium tungstate, alkali earth metal salts such as calcium tungstate and magnesium tungstate, Group VIII metal salts of tungstic acid such as cobalt tungstate, nickel tungstate, iron tungstate and copper tungstate.

Examples of heteropolyacids include phosphomolybdic acid, phosphotungstic acid, metal salts of these acids, and the like. The metal salts of heteropolyacids are not limited specifically and include Group VIII metal salts such as Co salt, Ni salt and Fe salt, Mg salt, Sr salt, Pb salt, Bi salt, etc. Among them, Group VIII metal salts are preferred, and Co salt is particularly preferred.

Among the above burning catalysts, CuO, CoO, NiO, $Ni_2O_3$, $MoO_3$, $WO_3$, oxygen-containing molybdenum compounds which form $MoO_3$ when heated, oxygen-containing tungsten compounds which form $WO_3$ when heated, cobalt phosphomolybdate, $Cr_2O_3$, $TiO_2$, SnO, ZnO, and $Fe_2O_3$ are particularly preferred, and CuO, CoO, NiO, $Ni_2O_3$, $MoO_3$, $WO_3$, Group VIII metal salts of molybdic acid and cobalt phosphomolybdate are still more preferred.

These burning catalysts can be used singly or as a mixture of two or more.

The particle size of the burning catalyst is not limited specifically, and can be properly selected from a wide range in accordance with, for example, the amount of the burning catalyst used, proportions to the other components, volume of the air bag and other conditions. The amount of the burning catalyst is not limited specifically, and can be properly selected in accordance with, for example, the proportions to the other components, volume of the air bag and other conditions.

The amount of the burning catalyst used varies depending on whether the oxohalogen acid salt and nitrate are used singly or in combination.

When the oxohalogen acid salt or nitrate is used singly as the oxidizing agent, it is suitable, for further reducing both CO and NOx, that the proportion of oxidizing agent be usually about 5 to about 150 wt. parts, preferably about 10 to about 120 wt. parts, more preferably about 30 to about 80 wt. parts per 100 wt. parts of the total amount of the gas generating base and oxidizing agent.

When the oxohalogen acid salt and nitrate are used in combination as the oxidizing agent, it is suitable, for further reducing CO and NOx, that the proportion of the oxidizing agent be usually about 0.1 to about 30 wt. parts, preferably about 0.5 to about 25 wt. parts, more preferably about 3 to about 15 wt. parts, per 100 wt. parts of the total amount of the gas generating base and oxidizing agent.

In the case of the oxygen-containing metal compound which forms a metal oxide when heated, it is used in an amount that forms the above specified amount of metal oxide.

Preferably, the air bag gas generating composition according to the present invention further contains a burning control agent. The burning control agent is used generally to decrease the burning temperature, to control the burning velocity and to prevent the gas generating agent from detonation caused by fire or strong impact in the course of production, transportation or storage.

The following (a) to (h), for example, can be used as the burning control agent.

(a) Simple metal substances such as B, Al, Mg, Ti, Zr, Mo, etc.

(b) Oxides, hydroxides, carbonates and bicarbonates of elements of the 2nd and 3rd periods in the periodic table such as Al, Mg, Si, B, etc. (preferably, $B_2O_3$, aluminum hydroxide, bentonite, alumina, diatomaceous earth, silicon dioxide, etc.)

(c) Carbonates, bicarbonates and oxides of alkali metals such as Na, K, etc.

(d) Carbonates and bicarbonates of alkali earth metals such as Ca, Mg, Ba, Sr, etc.

(e) Chlorides, carbonates and sulfates of other elements of the 4th to 6th periods in the periodic table than those mentioned in the above (a) to (c) (for example, Zn, Cu, Fe, Pb, Ti, V, Ce, Ho, Ca, Yb, etc.)

(f) Cellulose compounds such as carboxymethyl cellulose, hydroxymethyl cellulose, their ethers, microcrystalline cellulose powders, etc.

(g) Organic polymeric compounds such as soluble starch, polyvinyl alcohol, partially saponified products thereof, etc.

(h) Organic acids such as amino acids (e.g., glycine), ascorbic acid, citric acid, etc.

Among the above burning control agents, substances (a) to (d) and (h) are preferred, and simple metal substances such as B, Al, Ti and Z, metal oxides such as $B_2O_3$ and $Al_2O_3$, carbonates of alkali metals and alkali earth metals such as lithium carbonate, magnesium carbonate and calcium carbonate, metal hydroxides such as aluminum hydroxides and amino acids such as glycine are particularly preferred.

These burning control agents can be used singly or as a mixture of two or more. As the burning control agent, commercially available products may be used as such. The particle size thereof is not limited specifically, and can be properly selected from a wide range in accordance with, for example, the amount of the burning control agent used, proportions to the other components, volume of the air bag and other conditions.

When the burning control agent is used in the gas generating composition of the present invention, the amount thereof is not limited specifically, and can be properly selected from a wide range in accordance with the proportions to biscarbamoylhydrazine and the oxidizing agent, the kind of the burning control agent, kinds of other component, volume of the air bag and other conditions. It is suitable, however, to use the burning control agent in an amount of usually about 0.5 to about 50 wt. parts, preferably about 1 to about 30 wt. parts, more preferably about 3 to about 15 wt. parts, per 100 wt. parts of the total amount of biscarbamoylhydrazine and the oxidizing agent. When boron is used as the burning control agent, it is suitable to use said agent in an amount of about 0.5 to about 5 wt. parts, preferably about 1 to 3 wt. parts per 100 parts of the total amount of biscarbamoylhydrazine and oxidizing agent, for obtaining a lower burning temperature and appropriate burning velocity.

The air bag gas generating composition according to the present invention may contain a slagging agent. The slagging agent is an additive which solidifies the residue of the combustion of the gas generating agent, and thereby facilitates the removal of the residue with the filter in the air bag inflator. Known slagging agents are usable, which include, for example, silicon dioxide and alumina mentioned above as the burning control agent, boron oxide (in particular $B_2O_3$), etc. These slagging agents can be used singly or as a mixture of two or more. When the slagging agent is contained in the gas generating composition of the present invention, the amount thereof is not limited specifically, and can be properly selected from a wide range in accordance with the formulation of the gas generating composition and other conditions. For example, when silicon dioxide is used as the slagging agent, the molar ratio of the slagging agent to the oxidizing agent is preferably about 1/2. Also usable as the slagging agent are oxides containing alkali earth metals and alkali earth metal compounds which form oxides by reaction, for example, strontium oxide, strontium nitrate and the like.

Various additives conventionally used in this field can be further added in a range which does not adversely affect the advantageous characteristics of the gas generating composition of the present invention.

Further, in the present invention, at least one known oxidizing agent other than the nitrate and oxohalogen acid salt may be used in a range which does not adversely affect the advantageous characteristics of the gas generating composition of the present invention. Said optional oxidizing agent is not limited specifically, and can be properly selected from those conventionally used in this field. Preferred are those capable of generating and/or supplying oxygen at high temperatures, for example, nitrites, metallic peroxides, hyperoxides, ozone compounds, etc. Examples of nitrites include alkali metal salts such as lithium nitrite, sodium nitrite and potassium nitrite, alkali earth metal salts such as magnesium nitrite, barium nitrite and calcium nitrite. Examples of the metallic peroxides include alkali metal salts such as lithium peroxide, sodium peroxide, potassium peroxide and the like, alkali earth metal salts such as magnesium peroxide, calcium peroxide and barium peroxide, and the like. Examples of the hyperoxides include alkali metal compounds such as sodium hyperoxide, potassium hyperoxide and the like, alkali earth metal compounds such as calcium hyperoxide, strontium hyperoxide, barium hyperoxide and the like, rubidium hyperoxide, cesium hyperoxide and the like. Examples of the ozone compounds include compounds represented by the formula $MO_3$ wherein M is a Group Ia element such as Na, K, Rb, Cs or the like. In the present invention, metal sulfides such as molybdenum disulfide, bismuth-containing compounds, lead-containing compounds and the like can be used as the oxidizing agent. Commercially available product of these oxidizing agents may be used as such. The shape, particle size and the like of the oxidizing agent is not limited specifically, and can be properly selected in accordance with the amount of the oxidizing agent used, kinds and proportions of the other components, volume of the air bag and other conditions.

A preferable embodiment of the gas generating composition of the present invention may contain a slagging agent and other known additives.

According to the present invention, the gas generating base and/or at least one of the components other than the

gas generating base may be surface-treated with a coupling agent or chelating agent, for further improving the heat stability, facility of preparation and the like of the gas generating composition.

The coupling agent is not limited specifically and includes those conventionally known. Examples are silane-based coupling agents such as γ-aminopropyltriethoxysilane, γ-glycidyloxypropyltrimethoxysilane and methyltrimethoxysilane, titanate-based coupling agents such as isopropyltriisostearoyl titanate, aluminum-based coupling agents such as acetoalkoxyaluminum diisopropylate. Also, known chelating agents are usable. Examples are ethylenediamine tetraacetic acid (EDTA) and metal salts thereof (EDTA • disodium salt, EDTA • dipotassium salt, EDTA • dilithium salt, EDTA • diammonium salt, etc.), sodium diethyldithiocarbamate and the like. The surface treatment can be carried out by a conventional process comprising mixing the component to be treated and the coupling agent and/or chelating agent in a suitable solvent or without using solvents.

The gas generating composition of the present invention is produced by mixing biscarbamoylhydrazine, the oxidizing agent and other optional components in accordance with a conventional process.

The gas generating composition of the present invention can be prepared into a suitable shape. For example, a suitable amount of a binder is mixed with the gas generating composition of the present invention, and the mixture is tabletted and optionally dried. For the preparation, a solvent such as water or warm water is preferably added in a suitable amount to assure safety. Useful binders include, for example, those usually used for this purpose. The shape of the preparation is not critical and includes, for example, pellets, disks, balls, bars, hollow cylinders, confetti and tetrapods. It may be solid or porous (e.g. honeycomb-shaped). One or more projections may be formed on one or both surfaces of pellets or disks. The shape of projections is not limited specifically and includes, for example, cylinders, cones, polygonal cones, polygonal pillars, etc. Further, the size of preparation formed from the gas generating composition of the present invention is not specifically limited and can be properly selected from a wide range. However, for obtaining a still lower burning temperature and a more appropriate burning velocity, the suitable grain size of the preparation is about 0.3 to about 1.5 mm.

Alternatively, the respective components may be individually made into a preparation and the preparations may be used as mixed.

The preparation of the gas generating preparation of the present invention is placed into a container made of polyethylene or like synthetic resin or metal, whereby the gas generating preparation can be safely stored and transported.

The air bag gas generating composition of the present invention is not limited to automotive use and can be suitably used as a gas source for air bag systems to be installed in various transport means.

## Best Mode for Carrying out the Invention

The present invention is described below in more detail with reference to the following Examples, Comparative Examples and Test Examples. The manufacturers of the starting materials used in these examples are as follows unless otherwise specified.

Biscarbamoylhydrazine (BCH): product of Otsuka Kagaku K.K.
Azodicarbonamide (ADCA): product of Otsuka Kagaku K.K.
Potassium nitrate: product of Otsuka Kagaku K.K.
Potassium perchlorate: product of Nihon Carlit Co., Ltd.
Silicon dioxide: trade name "Nipseal NPS", product of Nippon Silica Co., Ltd.
Soluble starch (starch): Wako 1st grade product, product of Wako Pure Chemical Industries, Ltd.
CuO: specific surface area 48 $m^2/g$, average particle size about 7.4 μm, product of Nikki Chemical Co., Ltd.
$MoO_3$: product of Nippon Inorganic Colour & Chemical Co., Ltd.

In the following description, part(s) and percentage are all by weight, unless otherwise specified.

### Example 1

Thoroughly mixed together were powders of 45 parts of biscarbamoylhydrazine, 72.1 parts of potassium perchlorate, 10 parts of potassium nitrate, 10 parts of $MoO_3$ and 1 part of silicon dioxide. A 20% aqueous solution of soluble starch was added in an amount that provides a starch content of 3.5 parts, and the mixture was further stirred to give a wet powder. The wet powder was granulated using a granulating machine. The obtained wet granules were dried and compressed using a hydraulic tablet molding machine to give a pellet sample of a gas generating composition (6 mm in diameter, 3 mm in thickness and 0.15 g in weight).

### Example 2

A pellet sample of the gas generating composition of the present invention was prepared in the same manner as in

Example 1 with the exception that the amount of potassium perchlorate was changed to 67.7 parts and that 10 parts of CuO was used in place of $MoO_3$.

Comparative Example 1

Thoroughly mixed together were powders of 45 parts of azodicarbonamide, 56.3 parts of potassium perchlorate, 10 parts of potassium nitrate, 1 part of silicon dioxide and 6 parts of $MoO_3$. A 10% aqueous solution of soluble starch was added in an amount that provides a starch content of 1.5 parts, and the mixture was further stirred to give a wet powder. The wet powder was granulated by a granulating machine. The obtained granules were dried and compressed using a tablet molding machine to give a pellet sample of a gas generating composition (6 mm in diameter, 3 mm in thickness and 0.15 g in weight).

Test Example 1

A 0.3 mm-thick aluminum cup was charged with each of the pellet samples of the gas generating compositions obtained in Examples 1 and 2 and Comparative Example 1, and placed in the combustion chamber of an inflator having a gas outlet 7 mm in diameter and loaded with 0.8 g of boron/potassium nitrate as a transfer charge. The inflator was set in a 60-liter tank and actuated by applying the current, to thereby ignite the pellet sample of the gas generating composition. Then, the pressure and temperature in the inflator and the 60-liter tank were measured. After the burning, the gas in the 60-liter tank was collected into a tedlar bag and checked for the CO and NOx concentrations using a detector tube. The results are shown in Table 1.

The symbols in Table 1 stand for the following.

CP max: maximum pressure ($kgf/cm^2$) in the combustion chamber of the inflator
TP max: maximum pressure ($kgf/cm^2$) in the 60-liter tank, a parameter of the gas generating capability of the gas generating composition
tTP max: time (msec) in which the internal pressure of the 60-liter tank reaches the maximum, a parameter simulating the velocity of the inflation of the air bag
tTP 90: time (msec) in which the internal pressure of the 60-liter tank reaches 90% of the maximum, a parameter simulating the velocity of the inflation of the air bag

Table 1

| | Ex. 1 | Ex. 2 | Comp.Ex.1 |
|---|---|---|---|
| Amount (g) of pellet sample | 40 | 40 | 30 |
| CP max ($Kgf/cm^2$) | 102 | 102 | 62 |
| TP max ($kgf/cm^2$) | 1.2 | 1.4 | 0.7 |
| tTP max (msec.) | 28 | 60 | 250 |
| tTP 90 (msec.) | 17 | 30 | 170 |
| Tank temperature (°C) | 75 | 77 | 30 |
| CO concentration (%) | 0.48 | 0.50 | 0.65 |
| $CO_2$ concentration (%) | 7.4 | 7.3 | 5.5 |
| NOx concentration (ppm) | 1200 | 1500 | 1600 |

Table 1 reveals that the gas generating composition of the present invention exhibits equivalent burning velocity and is equivalently low in the concentration of toxic components such as CO and NOx in the after gas, to the gas generating composition comprising azodicarbonamide as the gas generating base.

Comparative Example 2

A pellet sample of the gas generating composition was prepared in the same manner as in Example 2 with the

exception that azodicarbonamide was used in place of biscarbamoylhydrazine.

Test Example 2

The pellet sample of the gas generating composition obtained in Example 2 was stored in a constant temperature vessel at 107°C for 400 hours. The remaining proportion (wt.%) was calculated to determine the degree of decomposition of the gas generating base. The remaining proportion of the gas generating composition of Example 2 was at least 99.5%, which proves that biscarbamoylhydrazine substantially did not decompose.

The remaining proportion (wt. %) of the gas generating composition of Comparative Example 2 was determined in the same manner as above with the exception that the storing time was 190 hours, and found to be 75%. It was proved that azodicarbonamide considerably decomposed, even in less than half of the storing time of the pellet sample of the gas generating composition according to the present invention.

It is apparent from these results that the gas generating composition of the present invention is much higher in heat stability than the gas generating composition comprising azodicarbonamide as the gas generating base.

Test Example 3

The burning temperature of the gas generating compositions of Example 2 and Comparative Example 2 was calculated by a simulation based on a thermal equilibrium calculation program of NASA (B.J. McBride, "CET89-Chemical Equilibrium with Transport Properties, 1989Com", COSMIC Program #LEW-15113, 1989, NASA, hereinafter referred to as "CET 89"). The burning temperatures of the gas generating composition of Example 2 and the gas generating composition of Comparative Example 2 were about 2100 K and about 2300 K, respectively.

As apparent from the above, the burning temperature of the gas generating composition of the present invention is lower by about 200 K than that of the gas generating composition comprising azodicarbonamide as the gas generating base.

Example 3

Using the components shown in Table 2 in the amounts (part) shown in the table, pellet samples of the gas generating compositions of the present invention were prepared in the same manner as in Example 1.

Table 2

| Sample No. | BCH | $KClO_4$ | Starch | $SiO_2$ | $KNO_3$ | Burning catalyst | |
|---|---|---|---|---|---|---|---|
| 1 | 45 | 67.70 | 3.5 | 1 | 10 | CuO | 10 |
| 2 | 45 | 62.15 | 3.0 | 1 | 10 | CuO | 10 |
| 3 | 45 | 72.05 | 3.0 | 1 | 10 | $MoO_3$ | 10 |
| 4 | 45 | 72.05 | 3.0 | 1 | 10 | $WO_3$ | 10 |
| 5 | 45 | 72.05 | 3.0 | 1 | 10 | ZnO | 10 |
| 6 | 45 | 72.05 | 3.0 | 1 | 10 | $Fe_2O_3$ | 10 |

Test Example 4

Using the pellet samples of the gas generating compositions of the present invention obtained in Example 3, the procedure of Test Example 1 was repeated to check the burning performance of the gas generating composition and the CO and NOx concentrations in the after gas. The results are shown in Table 3.

Table 3

| Sample | | CP max | TP max | tTP max | tTP 90 | T temp. °C | CO % | $CO_2$ % | NOx ppm |
|---|---|---|---|---|---|---|---|---|---|
| No. | Amount (g) | Kgf/cm$^2$ | | msec | | | | | |
| 1 | 40 | 150 | 1.8 | 26 | 15 | 118 | 0.36 | 7.7 | 1250 |
| 2 | 40 | 94 | 1.3 | 93 | 51 | - | 0.56 | 7.2 | 1550 |
| 3 | 40 | 110 | 1.0 | 420 | 191 | 79 | 0.55 | 7.1 | 1150 |
| 4 | 40 | 104 | 0.7 | 1292 | - | 63 | 0.53 | 7.2 | 1450 |
| 5 | 40 | 82 | 0.8 | 988 | - | 68 | 0.58 | 6.8 | 1350 |
| 6 | 40 | 100 | 0.8 | 22 | 13 | 80 | 0.75 | 7.0 | 1130 |

Table 3 shows that the gas generating composition of the present invention has excellent burning performance and the after gas of said composition has low CO and NOx concentrations.

Example 4 and Comparative Example 3

Using the components shown in Table 4 in the amounts (part) shown in the table, pellet samples of the gas generating compositions of the present invention were prepared in the same manner as in Example 1. In Table 4, samples Nos. 1 to 18 are gas generating compositions of Example 4, and samples Nos. 19 and 20 are those of Comparative Example 3 (as disclosed in DE-A-19,516,818).

Table 4

| Sample No. | BCH | $KClO_4$ | Starch | $SiO_2$ | $KNO_3$ | Burning catalyst | | Combustion adjusting agent | |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 45 | 59.10 | 3.0 | 1.0 | 20 | CuO | 10 | - | |
| 2 | 45 | 50.60 | 3.0 | 1.0 | 30 | CuO | 10 | - | |
| 3 | 45 | 42.00 | 3.0 | 1.0 | 40 | CuO | 10 | - | |
| 4 | 45 | 63.40 | 3.5 | 1.0 | 10 | CuO | 20 | - | |
| 5 | 45 | 72.00 | 3.5 | 1.0 | 10 | $MoO_3$ | 20 | - | |
| 6 | 45 | 71.80 | 5.0 | 1.0 | 10 | CuO | 10 | $MgCO_3$ | 10 |
| 7 | 45 | 71.80 | 5.0 | 1.0 | 10 | CuO | 10 | $B_2O_3$ | 5.5 |
| 8 | 45 | 72.00 | 3.5 | 1.0 | 10 | $MoO_3$ | 10 | $B_2O_3$ | 5.5 |
| 9 | 45 | 60.70 | 3.5 | 1.0 | 10 | CuO | 10 | $CaO_2$ | 20 |
| 10 | 45 | 73.80 | 5.0 | 1.0 | - | CuO | 25 | - | |
| 11 | 45 | 62.90 | 5.0 | 1.0 | - | CuO | 50 | - | |
| 12 | 45 | 52.00 | 5.0 | 1.0 | - | CuO | 75 | - | |
| 13 | 45 | 41.10 | 5.0 | 1.0 | - | CuO | 100 | - | |
| 14 | 45 | 63.30 | 5.0 | 1.0 | 10 | CuO | 20 | $Al(OH)_3$ | 10 |
| 15 | 45 | 76.20 | 3.5 | 1.0 | 10 | CuO | 10 | $CaCO_3$ | 10 |
| 16 | 45 | 76.20 | 3.5 | 1.0 | 10 | CuO | 10 | $LiCO_3$ | 10 |
| 17 | 45 | 76.25 | 3.5 | 1.0 | 10 | CuO | 10 | $Al(OH)_3$ | 10 |
| 18 | 45 | 76.25 | 3.5 | 1.0 | 10 | CuO | 10 | $CaCO_3$ | 10 |
| 19 | 45 | 80.60 | 3.5 | 1.0 | - | - | | $CaCO_3$ | 25 |
| 20 | 45 | 75.10 | 1.5 | 1.0 | - | - | | $CaCO_3$ | 20 |

Test Example 5

Using the pellet samples obtained in Example 4 and Comparative Example 3, the procedure of Test Example 1 was repeated to measure the burning performance of the gas generating composition and the CO and NOx concentrations in the after gas. The results are shown in Table 5.

Table 5

| Sample | | CPmax | TPmax | tTPmax | tTP90 | Ttemp. °C | CO % | $CO_2$ % | NOx ppm |
|---|---|---|---|---|---|---|---|---|---|
| No. | Amount (g) | Kgf/cm$^2$ | | msec | | | | | |
| 1 | 40 | 120 | 1.3 | 64 | 34 | 95 | 0.41 | 7.0 | 2500 |
| 2 | 40 | 104 | 1.0 | 115 | 57 | 78 | 0.34 | 6.8 | 2750 |
| 3 | 40 | 80 | 1.8 | 201 | 77 | 67 | 0.36 | 6.2 | 3500 |
| 4 | 40 | 88 | 1.2 | 76 | 36 | 87 | 0.37 | 8.0 | 1450 |
| 5 | 40 | 118 | 0.9 | 384 | - | 82 | 0.52 | 7.1 | >1200 |
| 6 | 40 | 46 | 0.7 | 24 | 16 | 56 | 0.68 | 7.7 | 1280 |
| 7 | 40 | 194 | 0.9 | 159 | 60 | 67 | 0.58 | 7.6 | 1500 |
| 8 | 40 | 158 | 0.6 | 1364 | - | 57 | 0.47 | 6.7 | 1700 |
| 9 | 40 | 118 | 1.1 | 74 | 26 | 80 | 0.52 | 7.4 | 1050 |
| 10 | 35 | 122 | 1.2 | 21 | 13 | 77 | 0.37 | 7.3 | 950 |
| 11 | 40 | 194 | 1.4 | 19 | 10 | 60 | 0.47 | 7.5 | 370 |
| 12 | 40 | 106 | 0.9 | 35 | - | 49 | 0.82 | 6.5 | 980 |
| 13 | 40 | 162 | 0.4 | 22 | - | 35 | 1.02 | 5.8 | 1650 |
| 14 | 40 | 196 | 1.4 | 19 | 9 | 86 | 0.38 | 6.7 | 1050 |
| 15 | 40 | 120 | 1.3 | 23 | 14 | 63 | 0.37 | 8.5 | 950 |
| 16 | 40 | 204 | 1.8 | 27 | 8 | 72 | 0.27 | 9.0 | 1200 |
| 17 | 40 | 82 | 0.7 | 16 | 12 | 52 | 0.60 | 6.9 | 800 |
| 18 | 40 | 122 | 0.8 | 23 | 14 | 65 | 0.61 | 9.0 | 700 |
| 19 | 40 | 86 | 0.1 | 42 | - | 33 | 0.35 | 2.0 | 200 |
| 20 | 40 | 100 | <0.1 | - | - | 25 | 0.16 | 1.2 | 120 |

It is apparent that the gas generating compositions of Comparative Example 3 (Samples Nos. 19 and 20) caused incomplete combustion, since said compositions have markedly low TP max values of 0.1 kgf/cm$^2$ or less and a $CO_2$ concentration of 2.0% or 1.2%.

Example 5 and Comparative Example 4

Using the components shown in Table 6 in the amounts (part) shown in the table, the procedure of Example 1 was repeated to prepare a pellet sample of the gas generating composition of the present invention (Example 5) and pellet sample of the gas generating composition disclosed in Japanese Unexamined Patent Publication No. 300383/1995 (Comparative Example 4). These compositions were tested for the following properties. The results are shown in Table 6.

1) Thermochemical calculation temperature (Tc)

The thermochemical calculation temperature (adiabatic flame temperature) of the gas generating composition based on a thermal equilibrium calculation program of NASA (CET89) was used as an index of the burning temperature.

2) DSC exothermic decomposition starting temperature (T DSC)

The exothermic decomposition starting temperature (T DSC) was measured by DSC (differential scanning calorimetry) to check the heat stability of the gas generating composition.

A gas generating composition is rated as thermally stable if the composition can exhibit the original gas generating performance even after being stored in an inflator maintained at 107°C for 400 hours. According to this measurement method, the heat stability of the gas generating composition was rated by a method comprising charging a canister with a gas generating composition, maintaining the canister at 107°C for 400°C and measuring the weight loss of said composition (heat loss test), as shown in Test Example 2.

The present inventors examined for the relation between the results of the heat loss test and the exothermal decomposition starting temperature (T DSC) determined by DSC (differential scanning calorimetry), and found that a gas generating composition with a T DSC of 473 K or more passes the heat loss test. Based on this finding, the heat stability of the gas generating composition was rated.

3) Strand burning velocity (r)

The gas generating composition was molded into strands in the form of square columns (7 mm x 7 mm x 30 mm). Each strand was coated with a restrictor, leaving one end uncoated, to prepare a sample. The sample was burned in a pressure vessel having an internal volume of about 1 liter under pressure of nitrogen (70 kg/cm$^2$) to record the time-pressure curve and calculate the linear burning velocity (mm/sec). The detonativity tends to increase as the linear burning velocity becomes higher.

4) Detonation propagativity

The detonation propagativity of the gas generating agent was determined by a United Nations-recommended gap test. The sample (gas generating composition) was placed in a steel drawn tube 40 mm in inner diameter and 48 in outer diameter. The tube was mounted with 160 g of pentlite (PETN/TNT = 50/50) booster and a No.6 electric detonator at the lower end, and with a 100 mm x 100 mm x 3 mm (thickness) mild steel panel as a proof panel at the upper end. An electric current was applied to the No. 6 electric detonator to explode the detonator and booster. Detonation propagativity of the samples was rated as "yes" when the steel tube was fragmented complately, and "no" when the steel tube was not fragmented completely and part of the sample remained unreacted.

Table 6

| | Example 5 | Comp. Ex. 4 |
|---|---|---|
| BCH | 16.8 | 37.0 |
| Potassium nitrate | 64.2 | - |
| Silicon dioxide | 14.0 | - |
| Soluble starch | 2.0 | - |
| Boron | 3.0 | - |
| Potassium perchlorate | - | 61.0 |
| Tc (K) | 1679 | 2371 |
| T DSC (K) | 538 | 535 |
| r (mm/s) | 3.9 (6.7 MPa) | 20.4 (7.0 MPa) |
| Detonation propagativity | Yes | No |

Table 6 reveals that the gas generating composition of the present invention has advantageous characteristics of low burning temperature, good heat stability, no detonativity and capability of maintaining the burning. On the other hand, the gas generating composition of Japanese Unexamined Patent Publication No. 300,383/1995, although having appropriate burning velocity and good heat stability, involves problems of a high burning velocity and detonativity.

Example 6

Using the components shown in Table 7 in the amounts (part) shown in the table, pellet samples of the gas generating compositions of the present invention was prepared in the same manner as in Example 1. Then, the procedure of Example 5 was repeated to check the obtained samples for the thermochemical calculation temperature (Tc) based on the thermal equilibrium calculation program of NASA (CET89), DSC exothermal decomposition starting temperature (T

DSC) and strand burning velocity (r). The results are shown in Table 7.

Table 7

| Formulation | | | | | T DSC (K) | r (70kg/cm$^2$) | Tc (K) |
|---|---|---|---|---|---|---|---|
| BCH | $KNO_3$ | Starch | $SiO_2$ | Boron | | | |
| 26.0 | 56.0 | 2.0 | 15.0 | 1.0 | 544.5 | 2.24 | 1746 |
| 23.9 | 58.0 | 2.0 | 13.9 | 2.0 | 542.5 | 2.66 | 1864 |
| 21.9 | 60.2 | 2.0 | 12.9 | 3.0 | 544.6 | 3.91 | 1982 |
| 19.8 | 62.3 | 2.0 | 11.9 | 4.0 | 547.5 | 5.56 | 2096 |
| 17.8 | 64.4 | 2.0 | 10.8 | 5.0 | 544.8 | 6.41 | 2212 |

Example 7

The procedure of Example 5 was repeated to check the DSC exothermal decomposition starting temperature (T DSC) and strand burning velocity of gas generating compositions each comprising 29 parts of hydrazodicarbonamide, 44 parts of potassium nitrate, 13 parts of silicon dioxide, 12 parts of potassium perchlorate, 5 parts of the burning catalyst shown in Table 8 and 3 parts of starch. The results are shown in Table 8.

Table 8

| Burning catalyst | r(mm/s) | T DSC (K) |
|---|---|---|
| $MoO_3$ | 16.8 | 517 |
| CuO | 7.4 | 541 |
| $CoMoO_4$ | 4.0 | 525 |
| $NiMoO_4$ | 3.7 | 526 |
| NiO | 3.6 | 539 |
| $SnO_2$ | 3.5 | 539 |
| None | 2.9 | - |

Table 8 reveals that the burning velocity is increased by the addition of a burning catalyst, in particular $MoO_3$ or CuO.

Example 8

The procedure of Example 5 was repeated to check the thermochemical calculation temperature (Tc) based on the thermal equilibrium calculation program of NASA (CET89) and the strand burning velocity of gas generating compositions comprising hydrazodicarbonamide, potassium nitrate, potassium perchlorate, silicon dioxide, starch and burning control agent in the amounts (wt. parts) shown in Table 9.

Table 9

| Formulation | | | | | | | r m/sec | Tc (K) |
|---|---|---|---|---|---|---|---|---|
| BCH | $KNO_3$ | $SiO_2$ | $KClO_4$ | Starch | Burning control agent | | | |
| 30.1 | 28.5 | 7.0 | 29.4 | 2.0 | Ti | 3 | 12.5 | 1667 |
| 31.0 | 26.6 | 7.1 | 30.2 | 2.0 | Zr | 3 | 18.3 | 1585 |
| 29.5 | 29.9 | 6.9 | 28.8 | 2.0 | Al | 3 | 13.2 | 1777 |
| 30.1 | 28.5 | 7.0 | 30.1 | 2.0 | Mg | 3 | 9.7 | 1714 |
| 31 | 33 | 10 | 24 | 2.0 | None | | 7.9 | 1447 |

Table 9 reveals that the burning velocity is increased by the addition of a burning control agent, in particular Zr, Al, Ti or the like.

Reference Example 1

70 g of biscarbamoylhydrazine was dispersed in 630 ml of water. A solution of 1.68 g of sodium aluminate (1% of alumina with respect to biscarbamoylhydrazine) in 70 ml of water was added dropwise over a period of 8 minutes with stirring. The obtained mixture was adjusted to pH 7 by dropwise addition of sulfuric acid (consisting of 1 part of concentrated sulfuric acid and 15 parts of water) over a period of 60 minutes. The mixture was further stirred for 30 minutes, and readjusted to pH 7 by dropwise addition of sulfuric acid. The resulting solids (biscarbamoylhydrazine) were collected by filtration, washed with water to remove sodium sulfate formed by the pH adjustment, and dried at 120°C for 1 hour. Then, biscarbamoylhydrazine was coarsely ground (10-mesh), giving modified biscarbamoylhydrazine. The modified biscarbamoylhydrazine presumably comprises aluminum hydroxide formed by the neutralization and attached to the surface of biscarbamoylhydrazine in a specific state. The BET specific surface area of the modified biscarbamoylhydrazine was 3.38 $m^2/g$, which was much greater than the BET specific surface area before the treatment (0.20 $m^2/g$).

Comparative Reference Example 1

70 g of biscarbamoylhydrazine was mixed with 1.07 g of aluminum hydroxide (theoretical amount of aluminum hydroxide formed by the neutralization of 1.68 g of sodium aluminate).

Comparative Reference Example 2

70 g of biscarbamoylhydrazine was mixed with 0.72 g of alumina (theoretical amount of alumina formed by heating 1.07 g of aluminum hydroxide to 200°C or more).

Test Example 6

0.3 g each of the modified biscarbamoylhydrazine of Reference Example 1, biscarbamoylhydrazine of Comparative Reference Examples 1 and 2 and untreated biscarbamoylhydrazine was individually placed in a mold 10 mm in diameter and 7 mm in depth (product of Ishitobi Manufacture Co. Ltd.) and a pestle was positioned on the mold, followed by compression under a pressure of 800 kgf to give a pellet. The pellet was set on a hardness tester (trade name "HARDNESS TESTER KHT-20N", product of Fujiwara Seisakusho K.K.) wherein the load on the pellet was gradually increased, and the load at which the pellet disintegrated was regarded as the hardness of the pellet. The hardness test was repeated several times to calculate the average value. The results are shown in Table 10.

Table 10

| BCH | Number of determinations | Hardness of pellet (kg) | R |
|---|---|---|---|
| Example 1 | 9 | 1.22 | 0.45 |
| Comp.Ex.1 | 9 | 0.55 | 0.35 |
| Comp.Ex.2 | 9 | 0.25 | 0.25 |
| Untreated | 9 | 0.45 | 0.30 |

In Table 10, "R" means the difference between the maximum and minimum determined values.

It is apparent from Table 10 that the surface-treated biscarbamoylhydrazine has remarkably improved moldability, compared with untreated biscarbamoylhydrazine or a mere mixture of biscarbamoylhydrazine and a surface treating agent.

Example 9

Thoroughly mixed together were powders of 45 parts of the modified biscarbamoylhydrazine of Reference Example 1, 72.1 parts of potassium perchlorate, 10 parts of potassium nitrate, 5 parts of molybdenum oxide and 1 part of silicon dioxide. A 20% aqueous solution of soluble starch was added in an amount that gives a starch content of 1.5 parts, and the mixture was further stirred to give a wet powder. The powder was granulated using a granulating machine, and the obtained wet granules were dried and compressed using a hydraulic tablet molding machine to give a pellet sample of an air bag gas generating composition (6 mm in diameter, 3 mm in thickness and 0.15 g in weight).

Example 10

A pellet sample of the gas generating composition of the present invention was prepared in the same manner as in Example 9 with the exception that the amount of potassium perchlorate was changed to 67.7 parts and that 10 parts of copper oxide was used in place of molybdenum oxide.

A comparative pellet sample of an air bag gas generating composition (6 mm in diameter, 3 mm in thickness and 0.15 g in weight) was prepared in the same manner as in Example 9 with the exception that unmodified biscarbamoylhydrazine was used.

Test Example 7

A 0.3 mm-thick aluminum cup was charged with each of the pellet samples of the gas generating compositions obtained in Examples 9 and 10 and a pellet sample of a gas generating composition prepared from unmodified biscarbamoylhydrazine, and placed in the combustion chamber of a inflator having a gas outlet 7 mm in diameter and loaded with 0.8 g of boron/potassium nitrate as a transfer charge. The inflator was set in a 60-liter tank and actuated by applying the current, to thereby ignite the pellet sample of the gas generating composition. Then, the pressure and temperature in the inflator and the 60-liter tank were measured. It was found that the pellet samples all generated the same degree of pressure and temperature. After the burning, the gas in the 60 liter tank was collected into a tedlar bag and checked for the CO and NOx concentrations using a detector tube. It was found that the pellet samples all produced after gas with the same degree of CO and NOx concentrations.

Reference Example 2

100 g of biscarbamoylhydrazine (product of Otsuka Kagaku K.K., BET specific surface area; 0.20 $m^2/g$, median diameter; 45.43 μm, the same applies hereinafter) was dispersed in 1 liter of water, and 25 ml of a 10% aqueous solution of carboxymethyl cellulose was added with stirring. The mixture was stirred with heating at 50°C for 2 hours. After completion of the stirring, precipitated biscarbamoylhydrazine was collected by filtration and dried at 80°C for 1 hour, giving modified biscarbamoylhydrazine.

Reference Example 3

100 g of biscarbamoylhydrazine was dispersed in 1 liter of water. To the dispersion were added 2.5 g of a 10% aqueous solution of carboxymethyl cellulose, 1 ml (about 1 g) of acrylic acid and 0.5 g of azobisvaleric acid, and the mixture was stirred with heating at 80°C for 2 hours. After completion of the stirring, precipitated biscarbamoylhydrazine was collected by filtration and dried at 80°C for 1 hour, giving modified biscarbamoylhydrazine.

Example 11

Thoroughly mixed together were powders of 45 parts of the modified biscarbamoylhydrazine of Reference Example 2, 72.1 parts of potassium perchlorate, 10 parts of potassium nitrate, 5 parts of molybdenum oxide and 1 part of silicon dioxide. A 20% aqueous solution of soluble starch was added in an amount that gives a starch content of 1.5 parts, and the mixture was further stirred to give a wet powder. The wet powder was granulated using a granulating machine, and the obtained wet granules were dried and compressed using a hydraulic tablet molding machine to give a pellet sample of an air bag gas generating composition (6 mm in diameter, 3 mm in thickness and 0.15 g in weight).

Example 12

A pellet sample of the air bag gas generating composition was prepared in the same manner as in Example 11 with the exception that the modified biscarbamoylhydrazine of Reference Example 3 was used in place of that of Reference Example 2.

A comparative pellet sample of an air bag gas generating composition was prepared in the same manner as in Example 11 with the exception that untreated biscarbamoylhydrazine was used.

Test Example 8

Three pellet samples of the gas generating compositions obtained in Examples 11 and 12 and a gas generating composition prepared from untreated biscarbamoylhydrazine were each set on a hardness tester (trade name "HARDNESS TESTER KHT-20N", product of Fujiwara Seisakusho K.K.) wherein the load on the pellet was gradually increased, and the load at which the pellet disintegrated was regarded as the hardness of the pellet. The hardness test was repeated several times to calculate the average value. The results are shown in Table 11.

Table 11

| BCH | Number of determinations | Hardness of pellet (kg) |
|---|---|---|
| Example 11 | 20 | 5.3 |
| Example 12 | 20 | 7.5 |
| Untreated | 20 | 2.8 |

Test Example 9

A 0.3 mm-thick aluminum cup was charged with each of the pellet sample of the gas generating compositions of Examples 11 and 12 and a pellet sample of a gas generating composition prepared from untreated biscarbamoylhydrazine, and placed in the combustion chamber of a inflator provided with a gas outlet 7 mm in diameter and loaded with 0.8 g of boron/potassium nitrate as a transfer charge. The inflator was set in a 60-liter tank and actuated by applying the current, to thereby ignite the pellet sample of the gas generating composition. Then, the pressure and temperature in the inflator and the 60-liter tank were measured. It was found that the pellet samples all generated the same degree of pressure and temperature. After the burning, the gas in the 60-liter tank was collected into a tedlar bag and checked for the CO and NOx concentrations using a detector tube. It was found that the pellet samples all produced after gas with the same degree of CO and NOx concentrations.

Reference Example 4

Biscarbamoylhydrazine (average particle size of 52 μm, BET specific surface area of 0.2 $m^2/g$, product of Otsuka

Kagaku K.K.) was ground with a counter jet mill. The conditions for the grinding were an air pressure of 6.5 kgf/cm$^2$, a velocity of 15,000 rpm and a feed rate of 5 kg/hr. Finely ground biscarbamoylhydrazine having an average particle size of 2 μm and a BET specific surface area of 8.0 m$^2$/g was thus prepared.

Reference Example 5

20 ml of water was gradually added to 100 g of finely ground biscarbamoylhydrazine obtained in Reference Example 4 on a granulating machine (trade name "HIGH SPEED MIXER", product of Fukae Kogyo K.K.), giving granules. The granules were dried at 80°C for 1 hour, giving granules of finely ground biscarbamoylhydrazine having an average grain size of 0.3 mm.

Example 13

Thoroughly mixed together were 45 parts of finely ground biscarbamoylhydrazine of Reference Example 4, 72.1 parts of potassium perchlorate, 10 parts of potassium nitrate, 5 parts of molybdenum oxide and 1 part of silicon dioxide. A 20% aqueous solution of soluble starch was added in an amount that gives a starch content of 1.5 part and the mixture was further stirred to give a wet powder. The powder was granulated using a granulating machine, and the obtained wet granules were dried and compressed using a hydraulic tablet molding machine to give a pellet sample (6 mm in diameter, 3 mm in thickness and 0.15 g in weight).

Example 14

A pellet sample of the gas generating composition of the present invention was prepared in the same manner as in Example 13 with the exception that the granules of Reference Example 5 was used in place of the finely ground biscarbamoylhydrazine of Reference Example 4.

A comparative pellet sample of an air bag gas generating composition was prepared in the same manner as in Example 13 with the exception that unground biscarbamoylhydrazine was used in place of the finely ground biscarbamoylhydrazine of Reference Example 4.

Test Example 10

The pellet samples of gas generating compositions obtained in Examples 13 and 14 and a pellet sample of a gas generating composition prepared from unground biscarbamoylhydrazine were each set on a hardness tester (trade name "HARDNESS TESTER KHT-20N", product of Fujiwara Seisakusho K.K.) wherein the load on the pellet was gradually increased, and the load at which the pellet disintegrated was regarded as the hardness of the pellet. The hardness test was repeated several times to calculate the average value. The results are shown in Table 12.

Table 12

| BCH | Number of determinations | Hardness of pellet (kg) |
|---|---|---|
| Example 13 | 20 | 6.7 |
| Example 14 | 20 | 5.9 |
| Unground | 20 | 2.8 |

Test Example 11

A 0.3 mm-thick aluminum cup was charged with 40 g of the pellet sample of the gas generating composition of Example 13 or 14 or a pellet sample of a gas generating composition prepared from unground biscarbamoylhydrazine, and placed in the combustion chamber of a inflator provided with a gas outlet 7 mm in diameter and loaded with 0.8 g of boron/potassium nitrate as a transfer charge. The inflator was set in a 60-liter tank and actuated by applying the current, to thereby ignite the pellet sample of the gas generating composition. Then, the pressure and temperature in the inflator and the 60-liter tank were measured. It was found that the pellet samples all generated the same degree of pressure and temperature. After the burning, the gas in the 60-liter tank was collected into a tedlar bag and checked for the CO and NOx concentrations using a detector tube. It was found that the pellet samples all produced after gas with the

same degree of CO and NOx concentrations.

## Claims

1. An air bag gas generating composition comprising, as active components, (1) biscarbamoylhydrazine as a gas generating base, (2) an oxohalogen acid salt as an oxidizing agent, (3) a nitrate as an oxidizing agent, and (4) a burning catalyst.

2. An air bag gas generating composition according to claim 1 which further comprises a burning control agent.

3. An air bag gas generating composition comprising (1) biscarbamoylhydrazine as a gas generating base, (2) an oxohalogen acid salt or a nitrate as an oxidizing agent, and (3) a burning catalyst.

4. An air bag gas generating composition according to claim 3 which further comprises a burning control agent.

5. An air bag gas generating composition according to claim 1 or 3 wherein biscarbamoylhydrazine is surface-treated with an inorganic surface treating agent, or surface-coated with a hydrophilic polymeric compound or a crosslinked product thereof, or finely ground.

6. An air bag gas generating composition according to claim 1 or 3 wherein the burning catalyst is at least one member selected from the group consisting of oxides of metals of the 4th to 6th periods in the periodic table, oxygen-containing metal compounds which form said metal oxides when heated, and heteropolyacids.

7. An air bag gas generating composition according to claim 1 wherein the proportion of the burning catalyst is 0.5 to 30 wt. parts per 100 wt. parts of the total amount of the gas generating base and oxidizing agent.

8. An air bag gas generating composition according to claim 3 wherein the proportion of the burning catalyst is 10 to 150 wt. parts per 100 wt. parts of the total amount of the gas generating base and oxidizing agent.

9. An air bag gas generating composition according to claim 2 or 4 wherein the burning control agent is at least one member selected from the group consisting of simple metal substances selected from B, Al, Mg, Ti, Zr or Mo, oxides, hydroxides, carbonates, bicarbonates of elements of the 2nd and 3rd periods in the periodic table (other than alkali metals and alkali earth metals), carbonates, bicarbonates and oxides of alkali metals, carbonates and bicarbonates of alkali earth metals, chlorides, carbonates and sulfates of other elements of the 4 to 6 periods in the periodic table than the above, cellulose compounds, organic polymeric compounds and organic carboxylic acids.

10. An air bag gas generating composition according to claim 1 or 3 which is molded into granules having a grain size of 0.3 to 1.5 mm.

## INTERNATIONAL SEARCH REPORT

International application No. PCT/JP96/02796

**A. CLASSIFICATION OF SUBJECT MATTER**

Int. Cl[6] C06D5/00, C06B43/00, 29/00, 31/00, 45/20, B60R21/26

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl[6] C06D5/00, C06B43/00, 29/00, 31/00, 45/20, B60R21/26

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho 1922 - 1996
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Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X<br>Y | WO, 95/00462, A1 (Automotive Systems Laboratory, Inc.), January 5, 1995 (05. 01. 95), Claims & JP, 8-500813, A & US, 5386775, A | 1, 3, 5, 7-8, 10<br>2, 4, 6, 9 |
| Y | JP, 7-223890, A (Nippon Koki Co., Ltd. and two others), August 22, 1995 (22. 08. 95), Claim; paragraphs (0011) to (0012), (0017) to (0018) & WO, 95/21805, A1 & EP, 694511, A1 | 1 - 10 |
| Y | JP, 6-239683, A (Daicel Chemical Industries, Ltd.), August 30, 1994 (30. 08. 94), Claim; paragraphs (0012) to (0016) (Family: none) | 1 - 10 |
| Y | JP, 6-227884, A (Nippon Koki Co., Ltd. and two others), August 16, 1994 (16. 08. 94), | 1 - 10 |

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:
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"P" document published prior to the international filing date but later than the priority date claimed
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| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| January 21, 1997 (21. 01. 97) | January 28, 1997 (28. 01. 97) |
| Name and mailing address of the ISA/<br>Japanese Patent Office<br>Facsimile No. | Authorized officer<br><br>Telephone No. |

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP96/02796

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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| Y | JP, 6-32690, A (Nippon Koki Co., Ltd. and two others), February 8, 1994 (08. 02. 94), Claim; paragraphs (0016) to (0021) & WO, 94/01381, A1 & EP, 607446, A1 | 1 - 10 |
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